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Stable-isotope geochemistry of the Pierina high-sulfidation Au–Ag deposit, Peru: influence of hydrodynamics on SO_4^{2-} – H_2S sulfur isotopic exchange in magmatic-steam and steam-heated environments

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Abstract

The Pierina high-sulfidation Au–Ag deposit formed 14.5 my ago in rhyolite ash flow tuffs that overlie porphyritic andesite and dacite lavas and are adjacent to a crosscutting and interfingering dacite flow dome complex. The distribution of alteration zones indicates that fluid flow in the lavas was largely confined to structures but was dispersed laterally in the tuffs because of a high primary and alteration-induced permeability. The lithologically controlled hydrodynamics created unusual fluid, temperature, and pH conditions that led to *complete* SO_4^{2-} – H_2S isotopic equilibration during the formation of some magmatic-steam and steam-heated alunite, a phenomenon not previously recognized in similar deposits.

Isotopic data for early magmatic hydrothermal and main-stage alunite ($\delta^{34}\text{S}=8.5\text{‰}$ to 31.7‰ ; $\delta^{18}\text{O}_{\text{SO}_4}=4.9\text{‰}$ to 16.5‰ ; $\delta^{18}\text{O}_{\text{OH}}=2.2\text{‰}$ to 14.4‰ ; $\delta\text{D}=-97\text{‰}$ to -39‰), sulfides ($\delta^{34}\text{S}=-3.0\text{‰}$ to 4.3‰), sulfur ($\delta^{34}\text{S}=-1.0\text{‰}$ to 1.1‰), and clay minerals ($\delta^{18}\text{O}=4.3\text{‰}$ to 12.5‰ ; $\delta\text{D}=-126\text{‰}$ to -81‰) are typical of high-sulfidation epithermal deposits. The data imply the following genetic elements for Pierina alteration–mineralization: (1) fluid and vapor exsolution from an *I*-type magma, (2) wallrock buffering and cooling of slowing rising vapors to generate a reduced ($\text{H}_2\text{S}/\text{SO}_4 \approx 6$) highly acidic condensate that mixed with meteoric water but retained a magmatic $\delta^{34}\text{S}_{\Sigma\text{S}}$ signature of $\sim 1\text{‰}$, (3) SO_2 disproportionation to HSO_4^- and H_2S between 320 and 180 °C, and (4) progressive neutralization of laterally migrating acid fluids to form a vuggy quartz→alunite–quartz±clay→intermediate argillic→propylitic alteration zoning.

Magmatic-steam alunite has higher $\delta^{34}\text{S}$ (8.5‰ to 23.2‰) and generally lower $\delta^{18}\text{O}_{\text{SO}_4}$ (1.0 to 11.5‰), $\delta^{18}\text{O}_{\text{OH}}$ (-3.4 to 5.9‰), and δD (-93 to -77‰) values than predicted on the basis of data from similar occurrences. These data and supporting fluid-inclusion gas chemistry imply that the rate of vapor ascent for this environment was unusually slow, which provided sufficient time for the uptake of groundwater and partial to *complete* SO_4^{2-} – H_2S isotopic exchange. The slow steam velocities were likely related to the dispersal of the steam column as it entered the tuffs and possibly to intermediate exsolution rates from magmatic brine. The low δD values may also partly reflect continuous degassing of the mineralizing magma. Similarly, data for

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steam-heated alunite ($\delta^{34}\text{S}=12.3\text{‰}$ to 27.2‰ ; $\delta^{18}\text{O}_{\text{SO}_4}=11.7\text{‰}$ to 13.0‰ ; $\delta^{18}\text{O}_{\text{OH}}=6.6\text{‰}$ to 9.4‰ ; $\delta\text{D}=-59\text{‰}$ to -42‰) are unusual and indicate a strong magmatic influence, relatively high temperatures (140 to 180 °C, based on $\Delta^{18}\text{O}_{\text{SO}_4\text{--OH}}$ fractionations), and partial to complete sulfur isotopic exchange between steam-heated sulfate and H_2S . Restricted lithologically controlled fluid flow in the host tuffs allowed magmatic condensate to supplant meteoric groundwater at the water table and create the high-temperature low-pH conditions that permitted unusually rapid $\text{SO}_4^{2-}\text{--H}_2\text{S}$ isotopic equilibration (50–300 days) and (or) long sulfate residence times for this environment. Late void-filling barite ($\delta^{34}\text{S}=7.4\text{‰}$ to 29.7‰ ; $\delta^{18}\text{O}_{\text{SO}_4}=-0.4\text{‰}$ to 15.1‰) and later void-filling goethite ($\delta^{18}\text{O}=-11.8\text{‰}$ to 0.2‰) document a transition from magmatic condensate to dominantly meteoric water in steam-heated fluids during cooling and collapse of the hydrothermal system. These steam-heated fluids oxidized the top ~300 m of the deposit by leaching sulfides, redistributing metals, and precipitating barite±acanthite±gold and goethite±hematite±gold. Steam-heated oxidation, rather than weathering, was critical to forming the orebody in that it not only released encapsulated gold but likely enriched the deposit to ore-grade Au concentrations.

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Keywords: Stable isotopes; High-sulfidation; Isotopic exchange; Steam-heated; Magmatic-steam; Pierina; Peru

1. Introduction

The Pierina Au–Ag deposit ranks as a world-class gold deposit with combined reserves and production totaling 251.9 t (8.1 Moz) of gold and 1518 t (48.8 Moz) silver at average grades of 2.24 and 13.46 g t⁻¹, respectively (Garay, E., 2002, written communication). Geological data reported in previous studies (Noble et al., 1997; Volkert et al., 1999; unpublished reports and maps, Barrick Gold Corporation) and in Rainbow et al. (this volume) and this study indicate that Pierina exhibits the principal characteristics of high-sulfidation epithermal Au–Ag deposits. The geological, geochemical, and genetic framework for such deposits is well established (e.g., Bethke, 1984; Stoffregen, 1987; White, 1991; Rye et al., 1992; Rye, 1993; Arribas, 1995; Giggenbach, 1997; Reed, 1997; Corbett and Leach, 1998; Hedenquist et al., 1998). Features that Pierina shares with other examples of this deposit type include a volcanic dome setting, volcanic host rock (ash flow tuffs), pyrite–enargite±covellite sulfide–sulfosalt assemblage, and vuggy quartz and quartz–alunite alteration. The magmatic–hydrothermal fluids responsible for alteration and mineralization are produced through the injection of magmatic volatiles into the epithermal environment. Pierina differs from similar deposits in having a relatively large volume of mineralized acid-sulfate-altered rock and an absence of major ore-bearing veins or breccia bodies, thus indicating an unusually high degree of lithological control relative to structural control of the alteration–mineralization process (see Fig. 1 of Sillitoe, 2000). Accordingly, the deposit

may be regarded as an end-member high-sulfidation epithermal deposit that provides an excellent opportunity to examine the interrelation of lithology, hydrodynamics, and fluid geochemistry.

In this study, we emphasize the stable-isotope systematics of the principal alteration and void-filling assemblages at Pierina and their implications for genetic processes and environments. Of particular interest are alunite, barite, and associated minerals in the magmatic–hydrothermal, steam-heated, and magmatic–steam environments (Rye et al., 1992). Specifically, we (1) characterize isotopically the major assemblages and fluid types in a space–time context, (2) evaluate the approach to mineral–fluid, alunite_{SO₄–OH}, and aqueous $\text{H}_2\text{S}\text{--SO}_4^{2-}$ isotopic equilibrium, (3) infer isotopic exchange rates and post-crystallization effects, (4) estimate the redox state for the hydrothermal fluids, and (5) propose a genetic model for alteration and mineralization at Pierina. A key finding of this study is that some steam-heated alunites and magmatic–steam alunites have stable-isotope signatures not previously recognized in other deposits. We propose that a lithological control of fluid flow restricted the ascent of magmatic vapor both in condensing form and expanding form to create the temperature–pH conditions for partial to complete $\text{H}_2\text{S}\text{--SO}_4^{2-}$ isotopic exchange. Furthermore, the isotopic characteristics of steam-heated alunite, barite, and goethite record the waning stage of hydrothermal activity when cooling and progressively more meteoric-dominant fluids oxidized the upper part of the deposit and likely enriched Au to ore-grade concentrations.

2. Deposit geology

The Pierina Au–Ag deposit is located on the eastern flank of the Cordillera Negra at 9°26.5'S, 77°35'W and between 3650 and 4200 m in elevation. Huaraz, the nearest major city, is ~10 km southeast of the deposit. Pierina is one of numerous Tertiary deposits in the Western Cordillera of central and northern Peru that defines nearly coincident arc-parallel metallogenic belts (Noble and McKee, 1999; Peterson, 1999). Metallogenesis was broadly related to intervals of magmatism along a western arc of plutonic, volcanic, and derivative epiclastic assemblages largely built on deformed and weakly metamorphosed Mesozoic shelf rocks exposed east of the Coastal batholith (Cobbing et al., 1981; Noble and McKee, 1999; Peterson, 1999).

The volcanic assemblage that hosts the Pierina deposit consists dominantly of calc-alkalic lavas, tuffs and pyroclastic breccias, subordinate amounts of epiclastic sandstones, conglomerates and breccias, and minor limestone (Cobbing et al., 1981; Noble and McKee, 1999; Strusievcz and Clark, 1998). The volcanic rocks are largely andesitic, although basalts are present and dacites or rhyolites are common in the upper part of the assemblage. These rocks have been variously referred to as the Calipuy Formation, Calipuy Group, the Llama-Calipuy, Tacaza, and Sillapaca volcanic sequences, Huaraz Group, and Chururo Group (e.g., Cobbing et al., 1981; Benavides-Cáceres, 1999; Noble and McKee, 1999; Strusievcz et al., 2000).

Details of the Pierina deposit geology summarized below are based on data from published and unpublished sources, as cited, and from field and laboratory investigations by the first author (RF) of this paper. The character and distribution of rock types and alteration assemblages were investigated through the mapping of selected mine areas, logging of 10.45 km of core from 60 exploration drillholes, study and description of 470 surface and core samples, and short-wave infrared (SWIR) analysis of 492 samples. Additional data on the mineralogy and paragenetic sequence were derived from the examination of 70 standard and polished thin sections, X-ray powder diffraction (XRD) analysis of 40 samples, and scanning electron microscope (SEM) and electron microprobe analysis of 17 samples.

Pierina is a subhorizontal stratabound Au–Ag deposit hosted almost entirely by ~16 Ma rhyolite ash

flow tuffs that overlie a footwall sequence of ~23 Ma andesite and dacite flows and intercalated minor pyroclastic and epiclastic units (Fig. 1; Strusievcz et al., 1999). Hydrothermal alunite from the deposit has been dated at 14.5 ± 0.4 Ma by the K/Ar method (Noble and McKee, 1999) and 14.56 ± 0.11 Ma (average of four samples) by the $^{40}\text{Ar}/^{39}\text{Ar}$ method (Strusievcz et al., 1998b). 'Sericite' from the low-sulfidation (Pb–Zn–Ag) Santo Toribio deposit approximately 4 km south of Pierina (Fig. 1) yielded dates between 14 and 16 Ma by the $^{40}\text{Ar}/^{39}\text{Ar}$ method (Strusievcz et al., 1998a).

At Pierina, the host rhyolite tuffs are up to 390 m thick in the area of the orebody and are characterized by feldspar, quartz, and biotite phenocrysts and xenocrysts and by lithic and collapsed pumice clasts in a siliceous altered–devitrified groundmass. Variations in clast type and abundance imply multiple ash flow units. Andesite porphyry with plagioclase feldspar, hornblende, and biotite phenocrysts is the dominant footwall lithology, although dacite porphyry of the same mineralogy plus sparse quartz also underlies the southern part of the deposit. Monolithic largely matrix-supported volcanic breccias consisting of footwall porphyry lithologies occur sporadically at the contact between the rhyolite tuffs and footwall sequence in the central and southern part the deposit (Fig. 2). Irregular to tabular bodies of hypabyssal quartz–feldspar–biotite porphyry (QFBP) intrude the footwall sequence and crosscut and interfinger with the rhyolite tuffs. One of the larger occurrences is situated immediately east and partly in fault contact with the deposit (Figs. 1 and 2). The QFBP bodies represent intrusive–extrusive flow dome complexes emplaced penecontemporaneously with the rhyolite tuffs. The geological relations suggest that the breccias, some of the tuffs, and domes developed in and marginal to a volcanic vent complex that is south of the deposit (Volkert et al., 1999) and was the source of relatively small phreatic and phreatomagmatic eruptions. The dome complex adjacent to the orebody may be the high-level manifestation of a mineralizing and perhaps mineralized intrusion at depth.

2.1. Alteration and void-filling sequence

The rhyolite tuffs and QFBP bodies in the mine area are typically pervasively altered to intermediate

Fig. 1. Bedrock geology in the Pierina–Santo Toribio area (modified from unpublished map, Barrick Gold Corporation). Also shown are the Pierina orebody and location of the cross-section depicted in Fig. 2.

and advanced argillic assemblages. The footwall andesite and dacite flows are propylitically altered except locally in the northern part of the deposit and along structures in the southern part of the deposit, where the flows are generally altered to argillic assemblages. This difference in alteration intensity and extent reflects a fundamental lithological control on fluid flow due to a contrast in permeability between the andesite–dacite flows and the rhyolite tuffs. Fluid flow was largely confined to structures in

the footwall porphyry sequence but was dispersed with a possible significant lateral component in the tuffs, as is suggested by the alteration patterns (Fig. 2).

Replacement, crustification, and crosscutting textures at the hand-specimen and outcrop scale record a paragenetic sequence of alteration and mineralization events that resulted in the Pierina deposit (Fig. 3). Spatial and textural relations among some of these alteration and void-filling assemblages are schemati-

Fig. 2. Cross-section through the Pierina deposit depicting rock types, alteration zones, faults, the lower limit of oxidation, and volume of rock containing $>0.5 \text{ g t}^{-1} \text{ Au}$. Data are based on the logging of core from the exploration drillholes indicated and on assays provided by Barrick Gold Corporation. Ppy—porphyry.

cally depicted in Fig. 4. Stage 1 is represented by a suite of magmatic-hydrothermal alteration assemblages broadly zoned outward in the succession: vuggy quartz $\rightarrow$ advanced argillic $\rightarrow$ intermediate argillic $\rightarrow$ propylitic. Unoxidized vuggy quartz alteration is sporadically preserved as small isolated sulfidic remnants in oxidized (sulfide absent) vuggy quartz (Fig. 4). The alteration is characterized by finely crystalline quartz, disseminated pyrite–enargite, and quartz-lined vugs containing Stage 2 assemblages, typically pyrite $\pm$ enargite, and later subspherical blebs of native sulfur. Vuggy quartz alteration overlaps and grades to an advanced argillic assemblage of alunite–quartz $\pm$ pyrophyllite $\pm$ dickite $\pm$ kaolinite (Fig. 2) that replaced pumice fragments, lithic clasts, phenocrysts–xenocrysts (except quartz), and the groundmass or matrix of volcanic rocks and hydrothermal breccias. Magmatic-hydrothermal alunite generally occurs as pink, platy, tabular, or bladed crystals up to $\sim 4 \text{ mm}$ long and,

in unoxidized rock, may be intergrown with pyrite. Alunite-bearing alteration grades to an intermediate argillic assemblage of dickite $\pm$ kaolinite $\pm$ illite $\pm$ illite/smectite that grades to a propylitic assemblage of chlorite–carbonate $\pm$ illite $\pm$ smectite. Both of these latter assemblages commonly include pyrite where unaffected by later oxidation. Limited textural evidence at the hand-specimen scale and the overlap of vuggy quartz and alunite–quartz $\pm$ clays at the deposit scale (Fig. 2) suggests that the alteration assemblages advanced outward by dissolution and replacement. Small areas of silicified rock are present in vuggy-quartz- and alunite–quartz-altered zones. This alteration type is characterized by massive microcrystalline (“cherty”) quartz that replaced rock matrix and filled vugs and intergranular pores.

Stage 2 of the paragenetic sequence consists of void-filling magmatic-hydrothermal assemblages that crosscut or overprint rocks altered during Stage 1

^a Clay minerals include kaolinite, dickite, pyrophyllite, illite, smectite, and illite/smectite.

Abbreviations: Goe–goethite; Hm–hematite; Jar–jarosite.

Fig. 3. Paragenetic sequence of the principal alteration and void-filling assemblages based on alteration, crosscutting, and crustification textures observed in outcrop, drill core, hand specimens, and thin sections. The Pierina deposit evolved from early acid sulfate alteration through a magmatic-hydrothermal void-filling phase to late oxidation characterized by steam-heated alunite, barite, and Fe oxides and hydroxides.

(Fig. 3). Metallization of the deposit was largely accomplished during this stage through the precipitation of most of the pyrite, enargite, gold, sphalerite, galena, and other trace metallic minerals in veins, hydrothermal breccias, and vugs of vuggy quartz and other rock types. However, some Au and other metals may have been transported by magmatic vapor (e.g., see Hedenquist et al., 1993) to the site of the deposit during Stage 1 alteration (Fig. 3), which might account for the low level of gold enrichment present in distal unoxidized altered rocks that apparently lack veinlets. Veins and hydrothermal breccias of Stage 2 are typically sparse, narrow, and discontinuous. Hydrothermal breccias are cemented with quartz–

sulfide or hematite–goethite derived from the oxidation of sulfides. Four vein-filling assemblages are recognized on the basis of the dominant mineral(s): Stage 2A, *quartz*±*pyrite*±*enargite*; Stage 2B, *alunite*±*clays*±*pyrite*±*enargite*; Stage 2C, *pyrite*–*enargite* and *sphalerite*–*galena*±*pyrite*; and Stage 2D, *clay*±*pyrite*±*enargite*±*covellite*±*chalcocite* (Fig. 3). The timing among these assemblages is poorly constrained because of a paucity of diagnostic crosscutting or crustification relations; however, limited observations imply a general temporal succession from stages 2A through 2C. The timing of Stage 2D clay veins is the least certain, although late clay coats vein cavities in several samples. Rare veins of granular or chalcidonic

Fig. 4. Spatial and textural relations among the principal alteration and mineralization assemblages depicted in a schematic cross-section of the deposit and in hypothetical hand-specimens that summarize observations from drill core and outcrop samples. Such relations form the basis of the paragenetic sequence presented in Fig. 3. Altn—alteration; QFB—quartz-feldspar-biotite.

quartz cut vuggy quartz rock in the upper levels of the deposit, whereas more common Stage 2A cockscomb quartz-sulfide and Stage 2C sulfide veins and hydrothermal breccias are present in all alteration zones, particularly deep and peripheral to the deposit. Stage 2B alunite-bearing veins are widely distributed in vuggy quartz and alunite-quartz alteration zones, whereas Stage 2D clay veins are present in alunite-quartz and intermediate argillic alteration zones. Vein alunite is white or pink and is generally finer-grained than the pink alteration alunite.

Stage 3 is represented by rare moderately to coarsely plumose alunite that fills veins and breccias in the deposit (Fig. 3). Two occurrences were analyzed: one consists of crudely layered pink alunite that apparently crosscuts fine-grained white Stage 2B alunite in a fault zone in the south-central part of the orebody (Fig. 4); the other is also crudely layered but forms the matrix to breccia in the QFBP body east of the ore deposit. Stage 3 alunite is later than Stage 1 alteration and probably

Stage 2 veins, but the age relative to other paragenetic stages is unclear. The monomineralic layered and coarsely plumose character of the Stage 3 void-filling alunite closely resembles the type-example magmatic-steam alunite of Marysville, UT, and it is on this geological basis that the Stage 3 alunite from Pierina is considered to be of magmatic-steam origin. Additionally, microprobe traverses across the Stage 3 samples revealed marked interlayer geochemical differences in wt.% Na₂O, K₂O, CaO, BaO, and F, as also documented for Marysville alunite (see Rye, *this volume*).

Stage 4 of the paragenetic sequence is an alunite-quartz±kaolinite assemblage (Fig. 3) with the characteristic features of steam-heated alteration (e.g., Sillitoe, 1993). The assemblage occurs in the upper part of the deposit (~3850 to 4150 m elevation) as a friable sandy quartz>alunite replacement of tuff and as an unconsolidated powdery alunite-quartz±kaolinite fracture-filling. The former occurrence is present along the western margin of the deposit, whereas the

latter type is common in N- and NE-striking faults and sheeted joints along the eastern margin of the deposit. Hematite and (or) goethite typically stain this assemblage red, red-brown, or yellow-brown, although it is unclear whether the Fe minerals are related to steam-heated alteration or later oxidation. Texturally, the steam-heated assemblage clearly supersedes the acid sulfate alteration of Stage 1, but its textural and temporal relation to other paragenetic stages is less certain. It seems likely that steam-heated alteration developed contemporaneously with Stages 1–3 but ultimately overprinted these assemblages.

Stage 5 is represented by a minor barite±acanthite±Fe oxide/hydroxide assemblage that fills veinlets and vugs primarily in oxidized vuggy quartz rock (Fig. 4). Rarely, barite crystals are encrusted with and partly replaced by quartz±pyrite. The Stage 5 assemblage is generally restricted to the upper levels (3850–4100 m) and northern half of the deposit. Most vuggy quartz rock is oxidized and contains little or no sulfide minerals except in small isolated remnants, as noted previously. Barite±acanthite veinlets with bleached halos cut these sulfidic remnants, indicating that the leaching of sulfides and native sulfur was at least partly accomplished by oxidizing fluids of Stage 5. The sulfidic remnants commonly have reaction rims of covellite±native silver that formed at the redox front between oxidized and reduced rock (Fig. 4). Near these boundaries, some vug-filling barite crystals are encased in late sulfur, which in turn is crosscut by or sparsely coated with covellite. Empirical observations, experimental data, and thermodynamic modeling indicate that sulfur forms as an immiscible liquid in magmatic acid sulfate fluids or as a sublimate from volcanic or hydrothermal gas (Kusakabe and Komoda, 1992; Reyes, 1991; Reed, 1997). Because sulfur crystallizes below ~119 °C, it is likely that early-formed sulfur either remains liquid or is melted and remobilized throughout most of the evolution of high-sulfidation epithermal systems (Vikre, 2000). Hence, textural relations for sulfur provide ambiguous paragenetic information (Vikre, 2000).

Stage 6 botryoidal auriferous goethite and goethite–hematite coat barite crystals and fractures, particularly in vuggy quartz rock, throughout the upper portion of the deposit (Fig. 4). Noble et al. (1997), Volkert et al. (1999), and Rainbow et al. (2000) suggested that auriferous hematite–goethite is of hypogene origin and

preceded barite deposition. However, where the minerals were observed in contact, botryoidal goethite and goethite–hematite, with one exception, cap the barite crystals. The oxidizing fluids of Stage 6 continued the leaching of sulfides and redistribution of metals that began with the overprinting of Stage 4 steam-heated alteration and progressed through Stage 5 barite±acanthite deposition.

2.2. Ore mineralogy, grades, and controls

Ore minerals at Pierina are dispersed through vuggy-quartz- and alunite–quartz-altered tuff, with ore-grade material largely confined to vuggy quartz zones. Most ore minerals are disseminated through altered rock or confined to veinlets and fracture coatings. Major semimassive to massive enargite-bearing veins or breccia bodies are lacking. Consequently, structural control of mineralization in the rhyolite tuff was not pronounced. Nonetheless, south of the deposit, several structures striking N 60–80°W and dipping 70–90°S localized fluid flow, hydrothermal brecciation, and vuggy quartz and alunite–quartz±pyrophyllite alteration and are expressed topographically as resistant ridges. Other recognized faults exhibit postmineralization displacements. A north-striking normal fault bounds the host tuff on the east, high-angle faults oriented N 55–70° E dissect the orebody into discrete blocks, and a north-dipping low-angle fault floors the north part of the orebody (this study; Tessier, 1998; Barrick Gold Corporation, unpublished maps). Tension crevices and landslide blocks on the steep hillside below and east of the mine indicate that mass movement is presently active.

Most Au is present as submicrometer particles of native gold (~2 wt.% Ag) associated with quartz, goethite, and hematite, whereas most Ag is present as aggregates (≤100 μm) of acanthite associated with quartz and barite (Barrick Gold Corporation, unpublished report). Acanthite has ~1450 ppm and ~65 ppm Au in solid solution and also contains rare inclusions of gold (Barrick Gold, unpublished report). Enargite has up to 8 wt.% Ag (Rainbow et al., 2000), 2.5 wt.% Sb, and 1.3 wt.% Sn (this study). Inclusions of pyrite, acanthite, galena, cassiterite, Zn-rich ksterite [Cu₂(Zn,Fe)SnS₄] and possibly jordanite [Pb₁₄As₆S₂₃] have been identified in enargite by microprobe analysis (this study).

Limited geochemical sampling of specific mineralized rock types indicates that alunite–quartz rock generally contains sub-ore grade concentrations of Au ($<0.5 \text{ g t}^{-1}$), sulfidic vuggy quartz rock contains ~ 1 to 2 g t^{-1} Au, and oxidized vuggy quartz rock contains ~ 3 to 6 g t^{-1} Au (McEwan, 1997; Noble et al., 1997; Garay, E., 2002, personal communication). Narrow veins of quartz, quartz–sulfide, and hydrothermal breccia have up to 5 g t^{-1} Au (Garay, E., 2002, personal communication). The late oxidation of the deposit leached Fe, Cu, Zn, and Cd and added Au, Ag, Hg, Pb, and Ba to vuggy-quartz-altered rocks (Noble et al., 1997). Sulfide leaching decreased the sulfide mineral content to $<0.5 \text{ vol.}\%$ sulfides within 100 m of the present surface but locally extended to depths of 300 m in permeable vuggy-quartz- and alunite–quartz-altered rock. The lower limit of oxidation approximately coincides with the contact between the rhyolite tuffs and andesite–dacite flows in the south–central part of the deposit (Fig. 2). The present water table in the mine area (5 to 55 m below surface) is generally well above this boundary.

3. Methods of isotopic analysis

The minerals and rocks analyzed isotopically were selected from drill core and surface samples to represent the space–time framework of the deposit. Separates of sulfide, quartz, barite, and native sulfur were prepared by handpicking, whereas clay mineral separates were prepared by handpicking, ultrasonic suspension, and elutriation. Alunite preparation followed the techniques of Wasserman et al. (1992) and included purification by HF-acid treatment and dissolution in NaOH followed by precipitation of BaSO_4 . Sample mineralogy and (or) purity was established by the methods noted previously (petrography, SWIR, XRD, SEM, microprobe). Carbon dioxide gas was produced from silicates and alunite (for total oxygen analysis) by reaction with BrF_5 using conventional methods (Taylor and Epstein, 1962; Clayton and Mayeda, 1963). Hydrous water was extracted from alunite and clay minerals by stepwise induction heating and was reacted with Zn granules at 500°C to generate H_2 gas. Sulfate+ V_2O_5 mixtures and sulfates alone were burned to produce SO_2 in a continuous gas flow system for sulfur and

sulfate oxygen isotopic analyses, respectively. Sulfur and oxygen isotopic analyses were performed on a Micromass OptimaTM mass spectrometer, and hydrogen isotopic analyses were performed on a Finnigan MAT 252TM mass spectrometer. Replicates generally reproduce to $\pm 0.2\text{‰}$ for sulfur, $\pm 0.2\text{‰}$ for oxygen prepared by the BrF_5 method, $\pm 0.5\text{‰}$ for sulfate oxygen prepared in the gas flow system, and $\pm 5\text{‰}$ for hydrogen. All analyses are reported using conventional notation and with respect to the standards SMOW for oxygen and hydrogen, and CDT for sulfur.

Isotopic calculations in this study were based on fractionation equations by Ohmoto and Lasaga (1982) for $\text{SO}_4(\text{solid and aqueous})\text{--H}_2\text{S}$; Ohmoto and Rye (1979) for sulfide– H_2S and sulfide–sulfide; Stoffregen et al. (1994) for alunite $\text{SO}_4\text{--H}_2\text{O}$, $\text{OH--H}_2\text{O}$ (both oxygen and hydrogen), and $\text{SO}_4\text{--OH}$; Matsuhisa et al. (1979) for quartz– H_2O ; Savin and Lee (1988) for pyrophyllite– H_2O oxygen; Sheppard and Gilg (1996) for kaolinite (dickite)– H_2O and illite– H_2O (both oxygen and hydrogen); and Gilg and Sheppard (1996) for kaolinite (dickite)– H_2O hydrogen.

4. Magmatic-hydrothermal alteration and void-filling

4.1. Quartz

The $\delta^{18}\text{O}$ values of vuggy quartz or silicified rock (11.1‰ to 15.7‰) are slightly higher than those of quartz phenocrysts (10.1‰ to 11.4‰) from QFBP and rhyolite tuff and are within the range of vein quartz or ‘chalcedony’ (8.8‰ to 17.1‰; Table 1). In general, quartz phenocrysts in altered igneous rocks retain their primary isotopic compositions and in unaltered igneous rocks of intermediate composition average 1‰ to 1.5‰ higher than whole-rock values (Taylor, 1968). This difference implies that primary $\delta^{18}\text{O}$ values for the Pierina host rocks were $\sim 8.5\text{‰}$ to 10.5‰ and that acid leaching and quartz druse development resulted in a 1‰ to 7‰ ^{18}O enrichment. Stage 2 vein quartz is further enriched by $\sim 1\text{‰}$ relative to coexisting vuggy quartz or silicified rock. These successive enrichments in ^{18}O likely reflect progressively lower temperatures of deposition for each type of quartz. If the vein quartz ($\delta^{18}\text{O}=8.8\text{‰}$ to 17.1‰) was precipitated from typical

Table 1

Oxygen and hydrogen isotopic values (in ‰) of rocks, silicates, oxides–hydroxides, and fluids, Pierina Au–Ag deposit, Peru

Sample	Location ^a	Elev (m)	Min ^b	Stage	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}_{\text{fl}}$	$\delta\text{D}_{\text{fl}}$	T °C ^c	Description
<i>Quartz and whole rocks</i>										
P-401	700S-200E	3977	Qz	ig	11.4					phenos, tuff; Al altn
P-455	600 m E. of mill		Qz	ig	10.1					phenos, QFP; Prop altn
P-3	1400S-1040E	4057	Qz	ig	10.5					phenos, QFP; Cl altn
P-362	100S-150E	3911	WR	1	14.5					VQz rk w/Qz druse
			Ch	2	15.2					vn: Ch-sulfide
P-355	200S-200E	3931	WR	1	11.1					VQz rk w/Qz druse; Al vnlt
			Qz	2	12.2					vnlt
P-56	550S-400E	3810	WR	1	14.9					VQz rk w/Qz druse
P-69	550S-400E	3740	WR	1	15.7					tuff; Sil
P-376b	50N-100E	3866	Ch	2	12.1					vn
P-371	50S-50E	3902	Qz	2	10.7					vnlt; Sil
P-312	350S-400E	3839	Qz	2	13.9					clast in fault
P-57	550S-400E	3804	Ch	2	15.1					vn; VQz altn
P-438	550S-450E	3833	Qz	2	16.4					stockwork: Qz–En
P-400	700S-200E	4053	Qz	2	17.1					vn: Qz<Al; Al altn
P-406	750S-600E	3777	Qz	2	8.8					vnlt; VQz halo->Di–Py altn
P-409	950S-1080E	3752	Qz	2	10.1					vn: Qz–sulfide; Al+VQz altn
P-411	1030S-1030E	4088	Qz	2	16.5					hydrothermal bx mx
<i>Clay minerals</i>										
P-74	600S-500E	3966	Il (Sm)	1	6.9	–109	–1.2	–84	175	rplmt: Il–(Sm) altn
P-266b	700S-300E	3973	Di (Ka)	1	4.9	–97	0.5	–80	200	rplmt: Di–(Ka–Al)–Py altn
P-382a	00N-00E	3793	Di (Ka)	1	3.2	–94	–1.2	–77	200	rplmt: Di (Ka) altn
P-286	750S-600E	3850	Di	1	5.8	–107	0.3	–89	200	rplmt: Di–(Al–Py) altn
P-135	700S-450E	4058	Il	1	8.5	–105	1.5	–80	200	rplmt: Il–Py altn
P-139	700S-450E B	3962	Il	1	6.6	–96	–0.4	–71	200	rplmt: Il–Py altn
P-310	350S-400E	3912	Il	1	7.1	–102	1.2	–77	200	rplmt: Il–Py altn
P-346	400S-100E G	3965	Ka	2	12.5	–81	–0.6	–57	100	vnlt; Stm-Htd? Al–Ka altn
P-409	950S-1080E	3752	Ka	2	9.9	–117	–3.2	–93	100	vn: Ka>Qz–Py–En; Al+VQz altn
P-149b	650S-650E	3703	Ka	2	10.1	–126	–3.0	–103	100	fbx: Ka–En
P-394b	800S-350E	3989	Ka (Di)	2	6.6	–126	–0.4	–107	175	vnlt: Ka–(Al–Di); Al altn
P-384	750S-500E B	3825	Ka (Il)	2	4.7	–114	–2.3	–96	175	vnlt: Ka–Il–Py; Ka–Il–Py altn
P-359	050N-300E	3769	Di	2	6.1	–113	–0.9	–95	175	vnlt; Di–Hm altn
P-265	750S-250E	3789	Di	2	4.3	–109	–2.7	–90	175	vnlt: Di>Al; Al–(Di–Ka)–Py altn
P-206	300S-600E	3746	Il	2	5.7	–110	–1.2	–85	200	vnlt: Il–Py; Il–Py altn
P-303	400S–800E	3865	Pyro	2	4.9	–96	0.7	–71	250	vnlt: Al–Pyro; Al–Pyro altn
<i>Goethite±hematite</i>										
P-379	00N-00E	3909	Goe	6	–11.8					bot Goe>barite; VQz rock
PB-1	150E-250E	3940	Goe	6	–8.7					bot Goe>barite; VQz rock
P-368	150S-100E	3919	Goe	6	0.2					bot Goe in fract; VQz rock
P-395	800S-300E	3985	Goe	6	–8.7					Goe±hm bx mx

Abbreviations (all tables): Al—alunite; altn—alteration; Ap—apatite; Ba—barite; bot—botryoidal; bx—breccia; Cl—clay; Cc—chalcocite; cgd—coarse-grained; Ch—‘chalcodony’; Cv—covellite; Di—dickite; En—enargite; fbx—fault breccia; FeOx—iron oxide/hydroxide; fgd—fine-grained; fl—fluid; fract—fracture; Gn—galena; Goe—goethite; Gyp—gypsum; Hm—hematite; ig—igneous; Il—illite; Ka—kaolinite; mgd—medium-grained; mx—matrix; p—pink; phenos—phenocrysts; Prop—propylitic; Py—pyrite; Pyro—pyrophyllite; QFP—quartz-feldspar porphyry; Qz—quartz; rplmt—replacement; S—sulfur; Stm-Htd—steam-heated; Sil—silicification; Sm—smectite; Sp—sphalerite; VQz—vuggy quartz; Vbx—volcanic breccia; vn—vein; vnlt—veinlet; w—white; WR—whole rock; xtls—crystals.

Symbols: ≠nonequilibrium; < earlier than; > later than.

^a Location of samples or sampled drillholes in mine coordinates.

^b Minor minerals in parentheses.

^c See text for basis of temperature estimates.

Pierina fluids ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = -4\text{‰}$ to 2‰ , determined below), then precipitation temperatures of 140 to 230 °C can be inferred from the quartz–H₂O fractionation equation of Matsuhisa et al. (1979).

4.2. Alunite and sulfides

Magmatic-hydrothermal alunite has variable $\delta^{34}\text{S}$ (8.5‰ to 31.7‰), $\delta^{18}\text{O}_{\text{SO}_4}$ (4.9‰ to 16.5‰), $\delta^{18}\text{O}_{\text{OH}}$ (2.2‰ to 14.4‰), and δD (−97‰ to −39‰) values, whereas most sulfides and native sulfur exhibit relatively uniform values of $-0.5 \pm 2.5\text{‰}$ and $0 \pm 1.1\text{‰}$, respectively (Table 2). Stage 1 alteration alunite and sulfides are isotopically indistinguishable from their Stage 2 void-filling counterparts. Such isotopic characteristics typify magmatic-hydrothermal alunite and sulfides in high-sulfidation Au–Ag deposits (Rye et al., 1992; compilations by Arribas, 1995; Corbett and Leach, 1998; Cooke and Simmons, 2000).

4.2.1. Sulfate–sulfide $\delta^{34}\text{S}$ equilibrium and thermometry

Sulfur isotopic fractionations between intergrown alunite and pyrite of Stages 1 and 2 yield calculated temperatures ranging from 180 to 320 °C and averaging 240 °C ($n=18$ pairs; Table 2). Such values are consistent with those determined by sulfur isotopic and (or) fluid-inclusion thermometry for other high-sulfidation Au–Ag deposits and with the efficacy of magmatic SO₂ disproportionation to H₂S+SO₄^{2−} below 400 °C (e.g., Bethke, 1984; Stoffregen, 1987; Rye et al., 1992). Although experimental data indicate sulfur isotopic exchange between aqueous sulfate and sulfide species is kinetically inhibited, rates of exchange reach a maximum at low pH at all temperatures (Ohmoto and Lasaga, 1982). For example, according to Ohmoto and Lasaga (1982), in the alunite-stable range of pH $\approx$ 2.5, the sulfate–sulfide isotopic equilibrium is approached in hours to days at 150 to 350 °C. These experimental results imply that alunite–pyrite isotopic equilibrium was closely approached or attained during the alteration and void-filling stages at Pierina, and the results corroborate the general reliability of sulfate–sulfide geothermometers in the magmatic-hydrothermal environment. As discussed by Rye (this volume), such sulfur isotopic equilibration is typical of magmatic-hydrothermal deposits and

is a function of the relatively slow ascent of a magmatic vapor plume.

4.2.2. $\delta^{18}\text{O}$ alunite_{SO₄–OH} equilibrium and thermometry

A comparison of measured alunite $\Delta^{18}\text{O}_{\text{SO}_4\text{–OH}}$ fractionations versus predicted $\Delta^{18}\text{O}_{\text{SO}_4\text{–OH}}$ fractionations based on alunite–pyrite sulfur isotopic thermometry suggests that oxygen isotopic equilibrium between SO₄^{2−} and OH was approximately attained and preserved in 7 of the 10 alunite samples of Stages 1 and 2 that were analyzed; that is, differences between measured and predicted values are $<2.5\text{‰}$. However, for only three of the seven samples are calculated temperatures based on $\Delta^{18}\text{O}_{\text{SO}_4\text{–OH}}$ fractionations within 25 °C of the temperatures based on $\Delta^{34}\text{S}_{\text{alunite–pyrite}}$ fractionations; the remaining samples differ by ± 70 to 90 °C.

Three of the ten alunite samples analyzed have unusually large $\delta^{18}\text{O}_{\text{OH}}$ values and, on the basis of $\Delta^{18}\text{O}_{\text{SO}_4\text{–OH}}$ fractionations, yield impossible temperatures. The $\delta^{18}\text{O}_{\text{SO}_4}$ and δD values of these samples, however, fall on a positive correlation trend of $\delta^{18}\text{O}_{\text{SO}_4}$ and δD values for most alunite samples (discussed below) and therefore do not seem to be unusual. These effects are likely related to retrograde O and H isotopic exchange between water and the OH radical in alunite. Over the temperature range of interest, $\Delta^{18}\text{O}_{\text{OH–H}_2\text{O}}$ fractionations for alunite are significant, and retrograde exchange can produce an appreciable increase in alunite $\delta^{18}\text{O}_{\text{OH}}$ values, whereas $\Delta\text{D}_{\text{OH–H}_2\text{O}}$ fractionations are small, and retrograde exchange produces only a minor change in alunite δD values (Rye et al., 1992). A significant change in the isotopic composition of the fluid (e.g., by mixing) during retrograde exchange is improbable because the data would require the fluids at each sample location to increase in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value while maintaining a nearly constant and different $\delta\text{D}_{\text{H}_2\text{O}}$ value. Sulfate oxygen in alunite is not highly susceptible to postdepositional exchange, and the $\delta^{18}\text{O}_{\text{SO}_4}$ values are generally considered to represent primary signatures acquired during precipitation. Assuming this to be the case, calculations using alunite $\delta^{18}\text{O}_{\text{OH}}$ values, predicted $\Delta^{18}\text{O}_{\text{SO}_4\text{–OH}}$ fractionations, and the oxygen isotopic fractionation equation for alunite_{OH–H₂O} (Stoffregen et al., 1994) suggest that OH retrograde exchange occurred down to

Table 2

Stable-isotope values (in ‰) of sulfur-bearing minerals and related fluids, Pierina Au–Ag deposit, Peru

Sample	Location ^a	Elev (m)	Min	Stage	δ ³⁴ S	δ ¹⁸ O _{SO₄}	δ ¹⁸ O _{OH}	δD _{OH}	δ ¹⁸ O _{fl(SO₄)}	δ ¹⁸ O _{fl(OH)}	δD _{fl}	T °C ^b	Description
<i>Apatite</i>													
P-455b	600 m E. of mill	3973	Ap	ig	1.7								clear, nonmagnetic xtls
			Ap	ig	1.9							dark, magnetic xtls	
			Ap	ig	3.4							dark, magnetic xtls	
			Ap	ig	3.6							dark, magnetic xtls	
<i>Alunite±pyrite</i>													
P-118	700S-400E	3826	Al	1	25.7	12.7	7.9	−83	2.8	2.3	−77	217	rplmt; VQz–Al–Py altn
			Py	1	−0.1								
P-141	700S-450E B	3895	Al	1	26.5	9.1		−78	−2.1		−72	194	rplmt; Al–Di–Py altn
			Py	1	−1.9								
P-150	650S-650E	3704	Al	1	24.0	6.6		−76	−3.0		−70	223	rplmt; Al–Py altn
			Py	1	−1.2								
P-157	700S-450E	3722	Al	1	27.3	10.0		−82	−2.3		−76	178	rplmt; Al–Py altn
			Py	1	−3.0								
P-179	650S-650E	3746	Al	1	29.9	10.4	4.1	−79	−0.6	−2.3	−73	198	rplmt; Al–Py altn
			Py	1	2.0								
P-117	700S-400E	3843	Al	1	23.8	5.1		−97	−4.0		−91	233	rplmt; Al–Di–Py altn
			Py	1	−0.4								
P-88	600S-500E	3819	Al	1	23.5	8.8		−75	−0.8		−69	223	rplmt; Al–Di–Py altn
			Py	1	−1.7								
P-293	500S-550E	3806	Al	1	17.6	9.3		−60	2.5		−50	290	rplmt; Al–Pyro–Py altn
			Py	1	−2.1								
P-60	550S-400E	3761	Al	1	19.2	4.9			−1.9			291	rplmt; Sil–Al–Py altn
			Py	1	−0.4								
P-120	700S-400E B	3805	Al	1	20.8	5.1		−51	−2.5		−39	269	rplmt; Al–Di–Py altn
			Py	1	−0.4								
P-180	650S-500E B	3741	Al	1	22.8							243	rplmt; Pyro–Al–Py altn
			Py	1	−0.5								
P-345	400S-100E G	3967	Al	1	22.0	8.5		−57	0.1		−51	<u>248</u>	rplmt; Al altn
P-394a	800S-300E	3993	Al	1	24.2	16.5	11.9	−39	7.0	6.6	−33	<u>225</u>	rplmt; Al altn
P-339	400S-200E	3969	Al	1	31.7	14.0	13.9	−44	0.2	5.4	−38	<u>156</u>	rplmt; Al altn
P-401	700S-200E	4006	Al	1	29.0	6.3			−6.0			<u>177</u>	rplmt; Al altn
													<Cl–Gyp vnlt
P-104	700S-400E B	4099	Al	1?	14.2	11.3	6.1	−62	−1.9	−2.0	−56	160	rplmt; Al–VQz altn
													<clay
P-284	650S-600E B	3696	Al	2	22.0	5.0	11.4	−83	−3.4	6.9	−74	248	vnlt: Al–Py; Al–Py altn
			Py	2	−0.9								
P-163	700S-450E	3618	Al	2	24.5	10.5	14.4	−68	0.8	9.0	−59	222	vn: Al–Py–S–En?
			Py	2	−0.8								
P-276	650S-650E	3681	Al	2	23.7	4.9		−75	−3.3		−67	253	vnlt: Al–Py; Al–Py altn
			Py	2	1.2								
P-212	450S-500E	3720	Al	2	22.1	9.8		−54	2.1		−43	265	vnlt: wAl–Di; Al–Pyro–Py altn
			Py	2	0.6								
P-211	450S-500E	3769	Al	2	21.5	8.0			−1.2			232	Vbx mx: Al–Di–Py
			Py	2	−2.8								
P-294	500S-550E	3756	Al	2	21.3	8.2			−0.6			241	Vbx mx: Al–Pyro–Py; Al–Py altn
			Py	2	−2.2								
P-Bx	950S-1080E	3753	Al	2	19.0	7.7			1.8			318	Vbx mx: pAl–Cl–Py
			Py	2	1.1								

Table 2 (continued)

Sample	Location ^a	Elev (m)	Min	Stage	$\delta^{34}\text{S}$	$\delta^{18}\text{O}_{\text{SO}_4}$	$\delta^{18}\text{O}_{\text{OH}}$	$\delta\text{D}_{\text{OH}}$	$\delta^{18}\text{O}_{\text{H}(\text{SO}_4)}$	$\delta^{18}\text{O}_{\text{H}(\text{OH})}$	$\delta\text{D}_{\text{H}}$	$T\text{ }^\circ\text{C}^b$	Description
P-278	650S-650E	3645	Al	2	27.1	12.6		–63	1.3		–57	193	vnlt: wAl; Al–Py altn
P-207	300S-600E	3727	Al	2	27.5	9.4	5.7	–70	–2.1	–1.0	–64	190	vnlt: wAl–Py<Cc; Al altn
P-61	550S-400E	3756	Al	2	29.4	11.9	6.4	–55	–0.6	–1.1	–49	174	vn/bx: pAl–Py (mgd, tabular); Sil
P-241-F	500S-500E	3910	Al	2	19.6	6.6	2.2	–72	–0.5	–1.3	–66	282	vn: wAl (fgd, powdery); cut by 241-C,-M
P-241-C	500S-500E		Al	3	21.1	7.2	–3.4	–93			–87		vn: pAl (cgd, plumose, layer 1)
P-241-M	500S-500E		Al	3	23.2	11.5	5.9	–77			–71		vn: pAl (mgd, plumose, layer 2)
P-452	400S-1575E	3600	Al	3	8.5	1.0	–2.3	–85			–79		vn/bx: pAl (cgd, plumose, layered); Al altn
P-344	400S-100E G	4028	Al	4	12.3	11.7			–7.6			160	rplmt; sugary Qz–(Al) altn
PSH-1	575S-875E	4010	Al	4	27.2	13.0	7.9	–51	–0.2	–0.1	–45	165	fract filling: powdery Al–(Qz–Hm)
PSH-2	750S-725E	4030	Al	4	25.0	12.0	6.6	–42	–2.1	–2.1	–36	153	fract filling: powdery Al–(Qz–Hm)
PSH-3	720S-420E	4040	Al	4	24.0	12.7	7.1	–48	–2.3	–2.2	–42	142	fract filling: powdery Al–(Qz–Hm)
PSH-4-F	750S-350E	4040	Al	4	22.2	11.8	6.9	–48	–0.5	–0.4	–42	178	vnlt: fgd Al–(Qz)
PSH-4-C			Al	4	15.8	12.3							vnlt: mgd Al–(Qz)
PSH-5	225S-225E	3910	Al	4	22.5	11.7	9.4	–59	–1.8	1.1	–53	160	fract filling: powdery Al–(Qz–Hm) altn
<i>Barite</i>													
P-379	00N-00E	3909	Ba	5	27.7	8.6							vug filling: Ba<bot Goe; VQz altn
P-380	00N-00E	3884	Ba	5	9.2	0.7							vug filling: Ba<FeOx; VQz altn
P-374	00N-100E	3880	Ba	5	28.2	9.9							vnlt: Ba<FeOx; Sil–VQ altn
P-376a	00N-100E	3864	Ba	5	13.5	0.5							vug; VQz altn
P-376b	50N-100E	3866	Ba	5	19.5	1.5							vug; Sil
P-363	100S-150E	3910	Ba	5	28.8	9.4							vnlt: VQz altn
P-451	050S-150E	3905	Ba	5	28.4	9.4							vug; VQz altn; Tunnel 2
PB-1	150E-250S	3940	Ba	5	27.6	10.7							vnlt: Ba<bot Goe; VQz altn
PB-2	150E-250S	3940	Ba	5	26.2	4.3							vnlt/vug: Ba<Qz–Py coating; VQz altn
P-341	400S-200E	3947	Ba	5	24.8	10.3							vnlt: Ba<FeOx; VQz altn
P-45	550S-400E	3942	Ba	5	29.0	4.9							vug; VQz altn
P-382b	750S-500E	3903	Ba	5	7.4	–0.4							vnlt: Ba<FeOx–Cl; Al–Cl altn
P-408	950S-1080E	3874	Ba	5	29.7	14.6							vnlt: Ba<FeOx; Al–Qz altn
<i>Sulfides</i>													
P-206	300S-600E	3746	Py	2	1.2								vn: Il–Py; Il–Py altn
P-252	550S-450E	3800	Py	2	–0.5								vn: Qz–Py; Al altn

(continued on next page)

Table 2 (continued)

Sample	Location ^a	Elev (m)	Min	Stage	$\delta^{34}\text{S}$	$\delta^{18}\text{O}_{\text{SO}_4}$	$\delta^{18}\text{O}_{\text{OH}}$	$\delta\text{D}_{\text{OH}}$	$\delta^{18}\text{O}_{\text{Al}(\text{SO}_4)}$	$\delta^{18}\text{O}_{\text{Al}(\text{OH})}$	$\delta\text{D}_{\text{Al}}$	T °C ^b	Description
P-154	700S-450E	3784	Py	2	−1.9								vn: Py; Al–Py altn
P-287	750S-600E	3776	Py	2	−2.4								vn: Py–En; Al–Py altn
P-437	600S-400E,	3775	Sp	2	0.2							187	vnlt: Sp–Gn–Py; Cl altn
			Gn	2	−2.7								
P-103	600S-400E	3775	Py	2	−0.2							366	vnlt: Gn–Py; Di altn
			Gn	2	−2.7								
P-295	500S-550E	3677	Gn	2	−22.9								vn: Gn–(Cl); Pyro–Py altn
P-69	550S-400E,	3739	Gn	2	−1.9								vn: Gn; Sil–(Al–Ka)–Py altn
P-407	750S-600E	3776	Py	2	−0.4								vn: Py–En; Al–Py altn
			En	2	−2.6								
P-405	750S-600E	3932	En	2	−2.8								vn: Qz–Py–En; Al–Pyro–Py altn
ABX-10	1350S-1540E	3746	Py	2	1.5								vn: En–Py
			En	2	0.5								
P-409	950S-1080E	3753	En	2	−2.5								vn: Qz–Py–En<clay; Al–VQz altn
P-175	650S-500E	3833	Py	2	−1.2								vug: Py<Cv rim; VQz altn
			Cv	5,6	0.0								
P-372	050S-050E	3870	Py	2	0.2								vug: Py<Cv rim; VQz altn
			Cv	5,6	4.3								
P-56	550S-400E	3810	Cv	5,6	0.5								Cv rim; VQz altn
<i>Sulfur</i>													
P-44	550S-400E	3948	S	5	−0.3								vug: S; VQz–Py altn
P-84	600S-500E	3884	S	5	−0.6								vug: S; VQz–Py altn
P-153	700S-450E	3790	S	5	1.0								vug: S; VQz–Py altn
P-250	550S-450E	3903	S	5	1.1								vug: S; VQz–Py altn
P-255	600S-400E	3931	S	5	−0.1								vug: S; VQz–Py altn
P-375	00N-100E	3871	S	5	−1.0								vug: S; VQz–Py altn
P-367	100S-100E	3895	S	5	0.2								vug: S; VQz–Py altn
P-367b	050N-100E	3866	S	5	0.3								vug: S; VQz–Py altn

See Table 1 for abbreviations.

^a Location of samples or sampled drillholes in mine coordinates.

^b Alunite temperatures in bold calculated from alunite–pyrite sulfur isotope fractionations, temperatures underlined estimated from alunite sulfur isotope values (see text), temperatures in bold italics calculated from alunite_{SO₄–OH} fractionations, and temperatures in plain italics are an average of those calculated for steam-heated (Stage 4) alunite. Sulfide temperatures calculated from sulfide–sulfide fractionations.

~100 °C for the three anomalous alunite samples. In summary, most of the analyzed magmatic-hydrothermal alunite samples were affected to a minor degree by retrograde O and H isotopic exchange in the hydroxyl radical, and, for reasons that are unclear, a few samples experienced significant exchange, although crystal size may be a factor. Similar results were reported for the Summitville deposit (Rye et al., 1990; Bethke et al., this volume).

4.2.3. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values of alunite-forming fluids

Both the $\delta^{18}\text{O}$ and δD values of the magmatic-hydrothermal alunite and the calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values of the alunite-forming fluids are positively correlated (Fig. 5). The temperatures used to calculate the fluid values were either directly or indirectly derived from alunite–pyrite sulfur isotopic fractionations (Table 2). For magmatic-hydrothermal

Fig. 5. Diagram of δD vs. $\delta^{18}O$ for alunite (SO_4^{2-}), clay minerals, and their parent fluids. The δD_{H_2O} and $\delta^{18}O_{H_2O}$ values were calculated using relevant temperatures and mineral–water fractionation equations (see text and Table 2). Also shown for reference are fields for felsic magmatic waters (Taylor, 1992) and volcanic vapor (Giggenbach, 1992) and lines for meteoric water and supergene kaolinite. The elongate field for alunite fluids implies the mixing of magmatic and meteoric fluids; the estimated composition of Pierina meteoric water 14.5 my ago is based on the projection of the best-fit regression line (arrows) for alunite fluid values to the meteoric water line. A possible ^{18}O shift in Pierina meteoric water compositions due to isotopic exchange with andesitic volcanic rocks is depicted by the dashed line.

alunite lacking coexisting pyrite (e.g., because of removal by later oxidation), temperatures were calculated indirectly from estimates of $\delta^{34}S_{pyrite}$ values obtained from measured $\delta^{34}S_{alunite}$ values and the equation for the regression line of alunite–pyrite data.

Fluids associated with the formation of magmatic-hydrothermal alunite range from large values (about -33‰ δD and 7‰ $\delta^{18}O$) to progressively lower values (about -90‰ δD and -5‰ $\delta^{18}O$) along a trend that suggests a mixing of magmatic fluid and unexchanged meteoric water (Fig. 6). The magmatic end member fluid isotopically resembles a fluid inferred to have equilibrated with felsic magma. A projection of the data trend to the meteoric water line implies an approximate meteoric groundwater composition of $\delta D = -140 \pm 15\text{‰}$ and $\delta^{18}O = -19 \pm 2\text{‰}$ at the time of Pierina mineralization 14.56 my ago. Although the actual isotopic composition of meteoric water at this time and location is unknown, the estimated δD value is similar to that determined for meteoric groundwater ($-125 \pm 25\text{‰}$ δD) present in the vicinity of several Andean Peruvian mineral deposits

during their formation in the Late Miocene (5–10 Ma) (Pasto Bueno, Landis and Rye, 1974; Casapalca, Rye and Sawkins, 1974; Colqui, Kamilli and Ohmoto, 1977; San Cristobal, Campbell et al., 1984; Julcani, Deen et al., 1994).

If simple mixing between meteoric and magmatic fluids is assumed, then the magmatic-hydrothermal alunite precipitated from magmatic-dominant (50–100%) fluids (Fig. 5). Deviations from the fluid mixing trend to lower $\delta^{18}O_{H_2O}$ values evident in a few compositions of alunite-forming fluid may be related to the involvement of steam-heated fluids or minor water–rock isotopic exchange.

4.2.4. Alunite $\delta^{34}S$ and $\delta^{18}O_{SO_4}$ relations

The distribution of magmatic hydrothermal alunite $\delta^{34}S$ – $\delta^{18}O_{SO_4}$ values is portrayed in Fig. 6 relative to the predicted compositions of magmatic-hydrothermal sulfate that equilibrated with a fluid of $\delta^{18}O = 7\text{‰}$, $\delta^{34}S_{\Sigma S} = 1\text{‰}$, and $H_2S/SO_4 = 6$ at temperatures of 150 to 400 °C (fluid parameters for Pierina as determined in this study). Oxygen isotopic fractionations for alunite

Fig. 6. Diagram of $\delta^{18}\text{O}_{\text{SO}_4}$ vs. $\delta^{34}\text{S}_{\text{SO}_4}$ for alunite and barite. Shown for reference are the calculated compositions of magmatic-hydrothermal SO_4^{2-} (dashed line) on the basis of $\delta^{34}\text{S}_{\Sigma\text{S}}=1\text{‰}$, $\text{H}_2\text{S}/\text{SO}_4^{2-}=6$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}=7\text{‰}$, and temperatures of 150 to 400 °C. The possible range of steam-heated sulfate (dotted field) in equilibrium with magmatic–meteoric waters of $\delta^{18}\text{O}_{\text{H}_2\text{O}}\leq 7\text{‰}$ and $\delta^{34}\text{S}_{\text{H}_2\text{S}}=-2\text{‰}$ is shown by the stippled field. Also illustrated are the shift to higher $\delta^{34}\text{S}_{\text{SO}_4}$ values with SO_4^{2-} – H_2S isotopic exchange for steam-heated alunite and the possible composition of steam-heated sulfate incorporated into isotopically light barite.

SO_4 – H_2O (Stoffregen et al., 1994) and for SO_4^{2-} – H_2O (Mizutani and Rafter, 1969) indicate that alunite $\delta^{18}\text{O}_{\text{SO}_4}$ values should be $\sim 2\text{‰}$ larger than those for aqueous sulfate at these temperatures. The Pierina alunite has predicted $\delta^{34}\text{S}$ values, but the $\delta^{18}\text{O}_{\text{SO}_4}$ values range up to 11‰ less than those of magmatic sulfate (Fig. 6). These less-than-predicted alunite $\delta^{18}\text{O}_{\text{SO}_4}$ values are consistent with the involvement of isotopically light meteoric water in the alunite-forming fluids, as noted previously.

4.3. Clay minerals

Alteration and void-filling kaolinite, dickite, and illite have similar $\delta^{18}\text{O}$ (4.3‰ to 12.5‰) but lower δD (–126‰ to –81‰) values than those of magmatic-hydrothermal alunite (Table 1, Fig. 5). Furthermore, the δD values of void-filling clay minerals (–126‰ to –109‰) are distinctly less than those of their alteration counterparts (–109‰ to –94‰). Fracture-filling pyrophyllite and a kaolinite of possible steam-heated origin have relatively high δD signatures (–96‰ and –81‰, respectively).

4.3.1. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values of clay-forming fluids

The temperatures of clay formation are poorly constrained. Therefore, the isotopic values of clay-forming fluids were calculated using temperatures based on the following assumptions and comparisons: (1) the temperatures were ≤ 250 °C, a typical value for magmatic-hydrothermal alunite formation, because most clay samples are later than or peripheral to alunite alteration; (2) temperatures were within the stability ranges of relevant clay minerals in geothermal–epithermal environments (e.g., Hedenquist et al., 2000); (3) temperatures were 25 °C lower for later fracture-filling clays than for their alteration counterparts (assuming overall cooling with time); and (4) ~ 100 °C for vug-filling and (or) distal kaolinite (Table 1). The results indicate that the clay-forming fluids had $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values equivalent to those of alunite-forming fluids rich in meteoric water but had generally lower $\delta\text{D}_{\text{H}_2\text{O}}$ values (Fig. 5). A similar isotopic relation between clay and alunite source fluids is observed at Summitville (Bethke et al., this volume) and possibly at Red Mountain (Bove et al., 1990).

As shown in Fig. 5, the field for clay-forming fluids is subparallel to that for alunite-forming fluids. However, the position and orientation of the field for clay-forming fluid is highly dependent on the assumed depositional temperatures. For example, assumed temperatures of 100 to 150 °C instead of 175 to 200 °C (Table 1) would position most clay-forming fluids on the fluid-mixing trend for alunite, as apparently was the case for clay-forming fluids at Lepanto (Hedenquist et al., 1998). Conversely, the use of temperatures for void-filling clays equivalent to those used for their alteration counterparts (Table 1) would generate a more vertically oriented field of clay-forming fluids (Fig. 5). Involvement of unexchanged meteoric water would generate a mixing trend similar to that of the alunite-forming fluids, whereas the involvement of meteoric water that had isotopically exchanged with volcanic rocks would generate a more nearly vertical trend (Fig. 5). A Pierina-like meteoric water can undergo a 17‰ positive shift in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and a minimal shift in $\delta\text{D}_{\text{H}_2\text{O}}$ (Fig. 5) if isotopic exchange with andesitic rocks occurs continuously during convection, the final temperature reaches ~300 °C, and the integrated water/rock mass ratio reaches ~1 (Fig. 6; see Fig. 6.16 of Field and Fifiarek, 1985). Regardless of the aforementioned uncertainties, the relatively low $\delta\text{D}_{\text{H}_2\text{O}}$ values of the clay-forming fluids clearly indicate mixtures of magmatic and meteoric fluids in which the magmatic component is generally smaller (30–65%) than that of the alunite-forming fluids (50–100%). However, it is unclear whether rocks in the intermediate argillic alteration zone distal to fluid conduits were saturated with unexchanged or exchanged meteoric groundwater, although both possibilities seem tenable.

5. Magmatic-steam alunite

Magmatic-steam alunite precipitating from a rapidly rising expanding vapor plume is expected to have magmatic δD values, $\delta^{34}\text{S}$ values similar to that of bulk sulfur in the hydrothermal system, $\delta^{18}\text{O}_{\text{SO}_4}$ values similar to those of magmatic-hydrothermal alunite, and $\delta^{18}\text{O}_{\text{OH}}$ values in equilibrium with the fluids, unless the OH has experienced retrograde

exchange (Rye et al., 1992; Rye, this volume). The Pierina magmatic-steam samples have compositions that do not completely meet any of these criteria. The δD values (–93‰, –85‰, –77‰) are 20‰ to 40‰ less than accepted magmatic values, and the $\delta^{34}\text{S}$ values (8.5‰, 21.1‰, 23.2‰) are 8‰ to 22‰ higher than the estimated value for bulk sulfur (1‰; Table 2). Similarly, the $\delta^{18}\text{O}_{\text{SO}_4}$ values (1.0‰, 7.2‰, 11.5‰) extend to ~4‰ less than those of any magmatic-hydrothermal alunite at Pierina, and the $\delta^{18}\text{O}_{\text{OH}}$ values (–3.4‰, –2.3‰, 5.9‰) extend to 4‰ to 5‰ less than those of any Pierina alunite (Table 2). Temperatures based on $\Delta^{18}\text{O}_{\text{SO}_4\text{--OH}}$ fractionations range from implausibly low (20 °C) to reasonable (150 and 320 °C) estimates for the high-level environment of the Pierina deposit. The isotopic disparities are greatest between the two analyzed occurrences of magmatic-steam alunite (P-241, P-452), although there are also pronounced differences for the two layers in one sample (P-241-C, -M) (Table 2). Moreover, the data for the gas chemistry of fluid inclusions indicate that sample P-241-C is typical of magmatic-hydrothermal alunite, whereas sample P-452 is transitional between magmatic-hydrothermal and magmatic-steam alunite (Landis and Rye, this volume). The unusual isotopic and gas chemistry of the Pierina magmatic-steam alunite implies unusual conditions for this depositional environment that influenced fluid composition and isotopic exchange, particularly among sulfur species.

6. Steam-heated alunite

Steam-heated alunite has variable $\delta^{34}\text{S}$ values (12.3‰ to 27.2‰) but has relatively uniform $\delta^{18}\text{O}_{\text{SO}_4}$ (12.1 ± 0.9 ‰), $\delta^{18}\text{O}_{\text{OH}}$ (8.0 ± 1.4 ‰), and δD (-55 ± 7 ‰) values (Table 2). Five of the seven samples analyzed are isotopically indistinguishable from magmatic-hydrothermal alunite.

6.1. $\delta^{18}\text{O}$ alunite_{SO₄–OH} equilibrium and thermometry

In steam-heated alunite, hydroxyl hydrogen and oxygen and sulfate oxygen readily achieve isotopic equilibrium with the parent fluid; the $\Delta^{18}\text{O}_{\text{SO}_4\text{--OH}}$ fractionations typically yield reasonable tempera-

tures for this environment (Rye et al., 1992; Rye, this volume). With one exception, the $\Delta^{18}\text{O}_{\text{SO}_4\text{--OH}}$ fractionations for steam-heated alunite samples at Pierina yield temperatures of 140 to 180 °C (Table 2). These temperatures overlap the upper range reported for the steam-heated environment (90 to 160 °C) and the lower range determined for the high-sulfidation magmatic-hydrothermal environment (150 to 350 °C; Rye et al., 1992; this study). These results suggest that oxygen isotopic equilibrium between SO_4^{2-} , OH, and fluid was generally attained in the steam-heated environment at Pierina.

6.2. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values of steam-heated fluids

The $\delta^{18}\text{O}_{\text{OH}}$ and δD values and oxygen isotopic temperatures (140 to 180 °C) for steam-heated alunite at Pierina indicate fluid compositions ($\delta\text{D}_{\text{H}_2\text{O}} = -46 \pm 10\text{‰}$; $\delta^{18}\text{O}_{\text{H}_2\text{O}} = -1 \pm 2\text{‰}$) similar to those of the magmatic-hydrothermal alunite parental fluids (Table 2; Fig. 5). The field of steam-heated fluids shown in Fig. 5 is drawn to encompass a clay-forming fluid (P-346: -0.6‰ and -57‰) and an alunite-forming fluid (P-104: -2.0‰ and -56‰) related to samples of possible steam-heated origin. The clay sample is a high-level vein kaolinite that is in proximity to steam-heated alteration and whose δD value is 20‰ higher than that of most other analyzed clays. The alunite sample was classified as a magmatic-hydrothermal type but has the $\delta^{34}\text{S}$ – $\delta^{18}\text{O}_{\text{SO}_4}$ signature of steam-heated alunite. These features suggest that the two samples, and possibly a few others, may have formed in the steam-heated environment or may have exchanged with steam-heated fluids. The similarity in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and particularly $\delta\text{D}_{\text{H}_2\text{O}}$ values of steam-heated and magmatic-hydrothermal fluids indicates a strong magmatic influence in the steam-heated environment.

6.3. Alunite $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ relations

Most of the analyzed steam-heated alunite samples from Pierina have $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values similar to those of magmatic-hydrothermal alunite, with two exceptions exhibiting relatively low $\delta^{34}\text{S}$ (12.3‰ and 15.8‰) values (Fig. 6). Moreover, a high-level magmatic-hydrothermal alunite (P-104) has a low $\delta^{34}\text{S}$ value (14.2‰), as well as $\delta^{18}\text{O}_{\text{SO}_4}$ and δD values,

and a $\Delta^{18}\text{O}_{\text{SO}_4\text{--OH}}$ -based temperature (160 °C) similar to those of steam-heated alunite (Table 2; Fig. 6). These three alunite samples with $\delta^{34}\text{S}$ values $<17\text{‰}$ and with $\delta^{18}\text{O}_{\text{SO}_4}$ values $>10\text{‰}$ contain sulfate that is unlikely to have been generated by magmatic-hydrothermal processes (that is, they plot to the left of the magmatic-hydrothermal sulfate line of Fig. 6). Oxidation of H_2S gas in the vadose zone produces sulfate with a $\delta^{34}\text{S}$ value approximating that of the source H_2S and which has a potentially wide range of $\delta^{18}\text{O}_{\text{SO}_4}$ values (Rye et al., 1992). For Pierina, such steam-heated sulfate would have a $\delta^{34}\text{S}_{\text{SO}_4}$ value $\approx -2 \pm 2\text{‰}$ on the basis of average $\delta^{34}\text{S}_{\text{sulfide}}$ values of $-0.5 \pm 2.5\text{‰}$ and would have a $\delta^{18}\text{O}_{\text{SO}_4}$ value that reflects formation in the presence of steam, steam condensate, and atmospheric oxygen (Fig. 6). The unusual compositions of the steam-heated alunite require that, following percolation to the water table, the sulfate generated in the vadose zone isotopically exchanged with aqueous or streaming H_2S and magmatic–meteoric fluids at temperatures of 140 to 180 °C. This exchange step enriched the sulfate in ^{34}S by 14‰ to 29‰ relative to the initial value (-2‰) and yielded a uniform $\delta^{18}\text{O}_{\text{SO}_4}$ value of $10 \pm 3\text{‰}$ (Fig. 7). The data suggest complete oxygen equilibration with magmatic-hydrothermal fluids and partial to complete sulfur isotopic equilibration with H_2S . If correct, this represents the first documentation of *complete* sulfur isotopic equilibration for steam-heated alunite and implies unusual conditions affecting the rates of isotopic exchange and the residence time of sulfate.

7. Barite filling

Pierina barite has variable and broadly correlated $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values of 7.4‰ to 29.7‰ and -0.4‰ to 15.1‰, respectively (Table 2; Fig. 6). Most analyzed samples of barite have sulfate isotopic values similar to those of the low-temperature magmatic-hydrothermal alunite, although several samples have distinctly lower $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values. The overall trend of the barite “field” suggests either the mixing of or a temporal shift between two end member sulfates, one derived from the near-surface oxidation of H_2S in the presence of dominantly meteoric fluids ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = -15\text{‰}$ to -12‰)

and the other with a strong magmatic influence (Fig. 6).

8. Goethite filling

The $\delta^{18}\text{O}$ values (-8.7‰ and -11.8‰) of botryoidal goethite that encrusts barite crystals in vugs of vuggy quartz rock are similar to that of goethite±hematite (-8.7‰), which replaced the quartz–sulfide matrix of a hydrothermal breccia, but the values are distinctly lower than that of a fracture-filling goethite (0.2‰) (Table 1). Experimental studies of oxygen isotopic fractionation in the goethite–water and hematite–water systems indicate that fractionations are relatively small at temperatures $\leq 140\text{ °C}$ (Clayton and Epstein, 1961; Yapp, 1990; Bao and Koch, 1999). A recent compilation by Bao and Koch (1999) of published results on experimentally determined $1000 \ln \alpha_{\text{goethite-H}_2\text{O}}$ temperature relations suggests fractionations of about -3‰ at 140 °C , about -2‰ at 100 °C , and about 0‰ at 50 °C (average of four studies). Goethite is a relatively low-temperature mineral for hydrothermal systems, and the fractionations cited above imply that the Pierina samples last equilibrated with fluids of $\delta^{18}\text{O}_{\text{H}_2\text{O}} \approx -10\text{‰}$, -7‰ , and 2‰ (Fig. 5). Goethite $\delta^{18}\text{O}$ values reflect isotopic exchange with ambient fluids during the maturation of initial Fe oxide precipitates (i.e., a gel or poorly ordered ferrihydrite) to goethite (Bao and Koch, 1999). Regardless of whether the goethite-forming ambient fluids differed isotopically from the goethite-forming parental fluids at Pierina, the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values estimated above suggest a spectrum of late fluids that varied from those with a magmatic signature to those with a significant meteoric component.

9. Sulfur source and speciation

9.1. Aqueous $\delta^{34}\text{S}_{\Sigma\text{S}}$ and $\text{H}_2\text{S}/\text{SO}_4$

The source(s) of the sulfur in the Pierina deposit can be interpreted from the $\delta^{34}\text{S}$ composition of total sulfur ($\delta^{34}\text{S}_{\Sigma\text{S}}$) in the magmatic-hydrothermal fluids. This parameter and the $\text{H}_2\text{S}/\text{SO}_4$ ratio of the fluids

may be derived from a $\delta^{34}\text{S}_{\text{alunite}}$ vs. $\delta^{34}\text{S}_{\text{pyrite}}$ plot of coexisting magmatic-hydrothermal alunite and pyrite (Fig. 7). The systematics for using δ – δ diagrams to interpret sulfate–sulfide sulfur isotopic exchange is a recent development (Ficarek, 2003) and is summarized herein; applications and discussions of $\delta_{\text{sulfate}} - \delta_{\text{sulfide}}$ diagrams are also presented elsewhere in this volume by Bethke and Rye, Field et al., and Rye. Modeling results indicate that, on δ – δ diagrams, a straight line of negative slope represents a covariation in $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values generated through $\text{SO}_4^{2-} - \text{H}_2\text{S}$ isotopic exchange over a range of temperatures provided that (1) the $\text{SO}_4/\text{H}_2\text{S}$ ratio remained constant, (2) the $\delta^{34}\text{S}_{\Sigma\text{S}}$ value remained constant, and (3) isotopic equilibrium in a two-phase closed system was attained or closely approached. The absolute value of the slope of the straight line is equivalent to R , the $\text{SO}_4/\text{H}_2\text{S}$ molar ratio. An array of R lines is shown in Fig. 7 for $\text{SO}_4^{2-} - \text{H}_2\text{S}$ isotopic exchange in a system in which $\delta^{34}\text{S}_{\Sigma\text{S}} = 0$. Isotherms plot as straight lines of $+1$ slope in δ – δ space (Gregory and Criss, 1986), as illustrated for alunite–pyrite equilibration between 200 and 400 °C in Fig. 7. A theoretical upper temperature limit is reached at $\Delta_{x-y} = 0$, which is the isotherm that passes through the origin. This isotherm represents a locus of points corresponding to different $\delta^{34}\text{S}_{\Sigma\text{S}}$ compositions and the convergence of their related linear arrays of constant R . For the example of $\delta^{34}\text{S}_{\Sigma\text{S}} = 0$, the related array converges on the origin (Fig. 7). Consequently, linear data trends with negative slopes can be used to estimate R (i.e., absolute value of slope $m=R$), and the intercept of the trend projection with the isotherm passing through the origin is an estimate of $\delta^{34}\text{S}_{\Sigma\text{S}}$, which may be read directly from the abscissa or ordinate axis.

The Pierina data on the $\delta^{34}\text{S}_{\text{sulfate}} - \delta^{34}\text{S}_{\text{sulfide}}$ diagram of Fig. 7 form a subhorizontal linear cluster that spans isotherms corresponding to the calculated temperatures of 180 – 320 °C . The data correlate poorly because of the limited range of $\delta^{34}\text{S}_{\text{pyrite}}$ relative to $\delta^{34}\text{S}_{\text{alunite}}$, and the determination of a representative trendline is particularly sensitive to uncertainties related to analytical accuracy and model assumptions (equilibrium isotopic exchange, constant R , constant $\delta^{34}\text{S}_{\Sigma\text{S}}$, closed-system behavior). A linear regression analysis of the Pierina data results in a best-fit line with a slight positive slope of 0.06 (not shown in

Fig. 7. Diagram of $\delta^{34}\text{S}_{\text{pyrite}}$ vs. $\delta^{34}\text{S}_{\text{alunite}}$ for coeval alunite–pyrite pairs; $\diamond$ represents the sample not included in the regression analysis. Solid lines of +1 slope represent alunite–pyrite fractionations and corresponding temperatures; the line of $\Delta^{34}\text{S}_{\text{alunite-pyrite}}=0$ represents a locus of $\delta^{34}\text{S}_{\Sigma\text{S}}$ points. The dotted line is the best-fit representation of the Pierina data, excluding one sample (see text), and has a slope equivalent to the absolute value of the $\text{SO}_4^{2-}/\text{H}_2\text{S}$ ratio (0.09) and an intercept with the 0 fractionation line equivalent to the $\delta^{34}\text{S}_{\Sigma\text{S}}$ value (+1‰; read from the abscissa or ordinate).

Fig. 7) and a derived $\delta^{34}\text{S}_{\Sigma\text{S}}$ value of -2.3 . Lines of positive slope on a $\delta^{34}\text{S}_{\text{sulfate}}-\delta^{34}\text{S}_{\text{sulfide}}$ diagram imply that one or more of the aforementioned model assumptions and related interpretations are invalid. In the Pierina data set, both the alunite and pyrite with the largest isotopic values are from the same sample, indicating isotopic disequilibrium or $\delta^{34}\text{S}_{\Sigma\text{S}}$ variability on a local scale (minerals with largest and *smallest* values should coexist if equilibrium exchange had prevailed). Disregarding this sample in a regression analysis results in a best-fit line with a *negative* slope of -0.09 ($\equiv |R|$) and an inferred $\delta^{34}\text{S}_{\Sigma\text{S}}$ value of $+1.0$ (Fig. 7). For nearly horizontal trends, the small effects of pyrite– H_2S fractionation (e.g., 1.1‰ at 320 °C to 2.0‰ at 180 °C) are most pronounced. Converting the values for Pierina pyrite to H_2S values at relevant temperatures yields a best-fit line with almost the same $\delta^{34}\text{S}_{\Sigma\text{S}}$ intercept as above but with a slightly larger slope (-0.16). Overall, the $\delta^{34}\text{S}$ compositions of

alunite–pyrite pairs from Pierina suggest equilibrium exchange over a temperature range of 180 to 320 °C from sulfide-dominant fluids (R or $X_{\text{SO}_4}/X_{\text{H}_2\text{S}} \approx 0.16$, $\equiv X_{\text{H}_2\text{S}}/X_{\text{SO}_4} \approx 6$) with $\delta^{34}\text{S}_{\Sigma\text{S}} \approx 1\text{‰}$.

10. Discussion

10.1. Early acid sulfate alteration

The isotopic systematics of early acid sulfate alteration at Pierina is similar to that documented at other high-sulfidation Au–Ag deposits and is consistent with the magmatic-hydrothermal genetic model (e.g., Bethke, 1984; Stoffregen, 1987; White, 1991; Rye et al., 1992; Rye, 1993; Arribas, 1995; Giggenbach, 1997; Corbett and Leach, 1998; Hedenquist et al., 1998). A mineralizing intrusion below the Pierina deposit likely crystallized from an *I*-type magma and

exsolved saline fluids that initially accumulated below the brittle–ductile transition (~ 400 °C isotherm). Magmatic vapor separating from the exsolved brine slowly ascended along structures and condensed into meteoric groundwater primarily at the level of the permeable rhyolite tuffs. Cooling and buffering of the rising fluids by Fe^{2+} in rocks below the tuffs (andesites and possibly Mesozoic sedimentary rocks) generated a reduced ($\text{H}_2\text{S}/\text{SO}_4 \approx 6$) highly acidic condensate with a $\delta^{34}\text{S}_{\text{SS}}$ value of $\sim 1\%$. Acid was generated through the dissociation of HCl and HF gasses and the disproportionation of SO_2 to H_2S and HSO_4^- at temperatures ranging from 320 to 180 °C. The alteration zonation resulted from a progressive neutralization of the acid fluids as they migrated away from fluid and vapor conduits now marked by zones of vuggy quartz. Thermodynamic modeling (e.g., Stoffregen, 1987; Reed, 1997) indicates that vuggy quartz forms through the extreme base leaching of rocks at a $\text{pH} \approx 1$ and that alunite–quartz–pyrophyllite is stable at a $\text{pH} \approx 2.5$, intermediate argillic assemblages at $\text{pH} \approx 4$, and propylitic assemblages at a $\text{pH} \approx 5.5$.

10.2. Void-filling ore fluids

A widely proposed model for high-sulfidation epithermal deposits suggests that main-stage ore mineralization results from the introduction of the degassed residual magmatic-hydrothermal brines that provided vapor for the early acid sulfate alteration (e.g., White, 1991; Corbett and Leach, 1998; Cooke and Simmons, 2000). The presence of such a fluid at Pierina is supported by the presence of rare high-salinity halite-bearing secondary inclusions in quartz phenocrysts and Stage 2 vein quartz. Because of degassing, these fluids are expected to be more saline, metal-rich, and reduced than the Stage 1 fluids. Vapor-rich inclusions are apparently associated with some high-salinity inclusions, which suggests that the brines boiled, at least temporarily. Nonetheless, the role of such brines and of boiling in the formation of the Pierina ore deposit remains largely unsubstantiated. Conversely, the isotopic similarity between Stage 1 alteration and Stage 2 void-filling minerals, particularly alunite and clay, suggests a compositional similarity between the fluids. Indeed, the occurrence of alunite-sulfide and

clay-sulfide veinlets in wallrocks of identical alteration assemblages suggests that some fracture filling and alteration formed nearly contemporaneously from the same fluids.

Temperature estimates based on isotopic fractionations for both Stage 1 and Stage 2 minerals do not reveal a systematic increase with depth as, for example, is evident at Summitville (Bethke et al., [this volume](#)). Rather, maximum temperatures apparently increase from ~ 180 °C above 4000 m to ≥ 290 °C at 3750 to 3800 m and then decrease to ~ 225 °C at around 3600 m (Fig. 8)). Such a thermal profile, if accurate, is suggestive of a fluid plume that formed when hot acidic fluids rising along structures in the lava porphyries encountered the permeable tuffs, slowed in velocity, and dispersed upward and outward. Cooler meteoric dominant groundwater would have been drawn into the plume near the tuff-lava contact, and significant lateral fluid flow possibly occurred along the strike of the orebody. These inferred hydrodynamics are consistent with the teardrop-shaped vuggy quartz zone in the south-central part of the deposit (Fig. 2) and with the relatively large volume of vuggy quartz rock in the deposit.

10.3. Magmatic-steam alunite

Magmatic-steam alunite develops from rapidly rising and expanding columns of steam that breach the surface, whereas magmatic-hydrothermal alunite results from slowly rising and condensing columns of magmatic steam. The unusual isotopic and fluid-inclusion gas chemistry of the Pierina magmatic-steam alunite may reflect intermediate rates of vapor transport rather than either end member case. The velocity of ascending magmatic steam is ultimately related to rates of vapor exsolution from magmatic brines and to the abundance and accessibility of structural conduits in the overlying rocks. Although rates of brine degassing at Pierina are unknown, the cross-sectional profile of the vuggy quartz zone and the permeability contrast between the rhyolite tuffs and andesite flows suggest that the column of steam was throttled and deflected upon entering the tuffs, wherein structures were less developed and permeable flow predominated. Lower steam velocities would allow for the

Fig. 8. Temperatures determined from isotopic fractionations plotted vs. elevation of sample. The data apparently represent a thermal profile formed during alteration of the host tuffs by fluids with a significant component of lateral flow.

incorporation of groundwater into the steam column and would provide sufficient residence time for sulfate to partly exchange isotopically with H_2S and H_2O . Such a mechanism explains the generally lower than predicted δD , $\delta^{18}\text{O}_{\text{SO}_4}$, and $\delta^{18}\text{O}_{\text{OH}}$ values, higher than predicted $\delta^{34}\text{S}$ values, and a gas chemistry reflecting mixed magmatic-hydrothermal and magmatic-steam fluids.

The low $\delta\text{D}_{\text{H}_2\text{O}}$ values also may partly or largely reflect continuous degassing of the mineralizing magma. Near the end of degassing, when magmatic-steam alunite commonly precipitates, this mechanism can produce a 20‰ to 40‰ decrease in $\delta\text{D}_{\text{steam}}$ values (e.g., see Taylor, 1986, 1988; Hedenquist et al., 1998; Deyell et al., this volume). Although the vapor is enriched in deuterium relative to the melt because of $\Delta\text{D}_{\text{fluid-melt}}$ fractionations of around 10‰ to 40‰, progressive degassing of a finite magma batch causes both melt and vapor to decrease in δD , a change potentially recorded in the steam precipitates.

10.4. Low-temperature oxidation of the deposit

Oxidation may be broadly regarded as a process that destroys sulfides and generates Fe oxides or hydroxides. Such oxidation at Pierina is most pronounced in the upper ~300 m of the deposit, between 3850 and 4150 m in elevation, and occurred late in the evolution of the deposit, possibly spanning a relatively lengthy interval of time. Oxidation was related to processes operating near a descending water table, including steam-heated alunite alteration, barite void-filling, and goethite-hematite precipitation. Although these processes are discussed in terms of distinct paragenetic stages, they represent a spectrum of gradational and overlapping geochemical environments formed during collapse of the hydrothermal system.

10.4.1. Steam-heated environment

The isotopic systematics of the Pierina steam-heated alunite, kaolinite, and related fluids indicate a dominant magmatic influence in the steam-heated

environment, as also observed at Tambo (Deyell et al., [this volume](#)) and Cactus (Rye et al., 1992). However, the general attainment of $\text{SO}_4\text{--H}_2\text{S}$ isotopic equilibrium evident in Pierina steam-heated alunite has not been previously documented in other deposits, suggesting that the sulfate created by the oxidation of H_2S in the vadose zone had unusually long residence times or underwent unusually rapid isotopic exchange with H_2S after percolation to the water table. Relationships among $\text{SO}_4\text{--H}_2\text{S}$ fractionation, temperature, pH, and rates of isotopic exchange are depicted in Fig. 2 of Rye ([this volume](#)), which is based on data and interpretations by Ohmoto and Lasaga (1982). The results indicate that $\text{SO}_4\text{--H}_2\text{S}$ isotopic equilibrium is approached in a minimum of 50 to 300 days in fluids of $\text{pH} \approx 2$ at 180–140 °C, the temperatures of steam-heated alteration at Pierina. These sulfur isotopic exchange rates overlap but generally exceed those in the steam-heated environment of the low-sulfidation Crofoot-Lewis Au–Ag deposit (Fig. 2 of Rye, [this volume](#)). Because the pH values of steam-heated fluids at Pierina and Crofoot-Lewis were similar (~ 2.5 , alunite-stable), the generally higher temperatures at Pierina must have resulted in relatively high isotopic exchange rates for this environment.

The high temperatures and magmatic isotopic signature of the Pierina steam-heated fluids suggest that condensed magmatic-hydrothermal fluids displaced meteoric groundwater in the host tuffs up to the water table. The combination of factors that could have led to this result includes a high rate of vapor injection into the groundwater, a low rate of groundwater recharge, and an intrinsically low discharge rate due to the absence of major structures that would have channeled flow to hot springs on the flanks of the deposit. Vapor condensation can ultimately transfer sufficient heat to the fluid phase to initiate boiling. This process and (or) noncondensing magmatic steam supplied H_2S and isotopically light sulfate to the vadose zone and groundwater near the water table. Such high-level vapor–fluid interactions apparently created the high-temperature low-pH steam-heated environment that promoted appreciable $\text{SO}_4^{2-}\text{--H}_2\text{S}$ isotopic exchange and the generation of isotopically heavy steam-heated sulfate.

The boiling of magmatic acid fluids can further enhance $\text{SO}_4^{2-}\text{--H}_2\text{S}$ isotopic exchange by decreasing the fluid pH (Reed, 1997). A pH temporarily below

that of alunite stability (<2) would have the dual effect of increased isotopic exchange rates (Ohmoto and Lasaga, 1982) and, in the absence of a precipitating sulfate mineral, increased sulfate residence times. A very low pH may be attained in siliceous rocks with little buffering capacity, such as those produced by vuggy quartz alteration or intense steam-heated alteration along faults. Consequently, a lowering of the steam-heated environment into vuggy quartz rock would have been particularly conducive to the attainment of $\text{SO}_4^{2-}\text{--H}_2\text{S}$ equilibrium in the steam-heated fluids at Pierina.

10.4.2. Late barite filling

The concave-up J-shaped form of the barite field in Fig. 6 implies the mixing of two fluids with isotopically distinct sulfate in unequal concentrations. The isotopically light end member sulfate most likely formed in a steam-heated meteoric-water-dominant environment, whereas the isotopically heavy end member sulfate has a strong magmatic-hydrothermal signature. Assuming the isotopically light barite ($\delta^{18}\text{O} \approx 0\text{‰}$) precipitated at ~ 160 °C, a temperature typical of the steam-heated environment, then the fluid for this end member barite had a $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value of approximately -9‰ , a composition similar to that of some goethite-forming fluids. Modeling the shape of the barite field in Fig. 6 as a mixing curve suggests that magmatic-hydrothermal sulfate was approximately 10 times more concentrated than the steam-heated sulfate in their respective end member fluids (see Ohmoto and Goldhaber, 1997 for relevant equations). However, the low solubility of barite under most hydrothermal conditions indicates that appreciable amounts of Ba and SO_4^{2-} were not transported together in either end member fluid; barite precipitation typically is in response to the mixing of a Ba-rich fluid and a SO_4^{2-} -rich fluid (Holland and Malinin, 1979). At Pierina, Ba may have been supplied to barite depositional sites near the level of the water table either by a sulfate-deficient third fluid, which seems implausible, or by magmatic vapors. Evidence for the transport of Ba in magmatic vapors is provided by data from Tambo (Deyell et al., [this volume](#)), modern stratovolcanoes (Zimbleman et al., [this volume](#)) and the sawtooth variations in Ba concentrations in Marysville magmatic-steam alunite (Rye, [this volume](#)).

The presence at Pierina of steam-heated sulfate with magmatic-hydrothermal isotopic signatures provides another possible explanation for the barite data. At low water/rock ratios, magmatic acid sulfate fluids may evolve through water–rock reactions to a reduced fluid deficient in SO_4^{2-} , with substantial Ba derived from the leaching of earlier precipitated *alteration* barite and with significant concentrations of Ag and lesser Au (Reed, 1997). Such a fluid may have mixed with steam-heated fluids to generate the late *void-filling* barite $\pm$ acanthite at Pierina. In this case, the barite data may record the transition from an early isotopically heavy steam-heated sulfate that had equilibrated with magmatic-hydrothermal fluids at the water table to a later isotopically light steam-heated sulfate that underwent minimal SO_4^{2-} – H_2S exchange in cooler meteoric-water-dominant fluids. Consequently, the J-shaped field of barite data in Fig. 6 would not represent a mixing trend involving two distinct sources of sulfate but a temporal shift in the isotopic composition of sulfate derived from a single (steam-heated) source. Moreover, in the analyzed suite of samples, barite with low isotopic values is generally at lower elevations than barite with high isotopic values (Table 2), which suggests that a dropping water table accompanied the transition to meteoric-dominant fluids and the collapse of the system. A steam-heated origin for barite is consistent with its high-level distribution in the northern part of the deposit and with the reported occurrence of minor barite in steam-heated alteration zones at the Steamboat Springs (Sigvaldson and White, 1962) and Roosevelt Hot Springs (Parry et al., 1980) geothermal fields.

10.4.3. Late botryoidal goethite

Auriferous botryoidal goethite $\pm$ hematite generally superseded barite and sulfur at Pierina. Temperatures continued to decrease during the waning phase of hydrothermal activity, and most goethite likely crystallized at $<119^\circ\text{C}$, the temperature of sulfur crystallization. The range of goethite $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values from 2‰ to -10 ‰ apparently represents variable amounts of meteoric water in the steam-heated fluids, with the heavier value approximating that of fluids formed when magmatic condensate filled the tuff aquifer. The lowest $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values indicate the highest component of meteoric water inferred for the fluid evolution of the deposit, but they do not resemble the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value

estimated for unexchanged meteoric water (about -19 ‰) that might be expected during weathering of the deposit. Instead, the values record a late low-temperature supergene fluid that formed during the transition from the hydrothermal environment to the weathering environment.

Collectively, the data for steam-heated alunite, barite, and goethite document the waning of hydrothermal activity and the progressive influx of meteoric water at the top and margins of the system at Pierina. A relative drop in the water table during this interval is consistent with the large vertical extent of oxidized rock (~ 300 m), approximately planar lower limit of oxidation (Garay, E., 2002, personal communication; Fig. 2) and the barite compositions noted above. Oxidation mobilized and redistributed the Au, Ag, As, and Hg originally dispersed in sulfides and sulfosalts and supplied to the epithermal environment by magmatic vapors and brines. Although element fluxes specifically related to this redistribution process are poorly constrained, the overprinting of low-grade sulfidic rock by steam-heated alteration is capable of producing economically important enrichments in Au, as documented for the Crofoot-Lewis deposit (Ebert and Rye, 1997). Similarly, supergene steam-heated oxidation at Pierina may not only have liberated encapsulated gold but may also have enriched low-grade material to ore-grade Au concentrations. In general, late oxidation may be the critical process for producing ore at disseminated low-grade Au–Ag high-sulfidation deposits.

11. Summary

The dominant lithological control exerted on the hydrodynamics of alteration–mineralization at the Pierina deposit is linked to the isotopic signatures of alunite and barite through fluid mixing and the kinetics of SO_4^{2-} – H_2S isotopic exchange. A high primary and alteration-induced permeability and paucity of major structures resulted in slow dispersed lateral fluid flow in the host rhyolite tuffs relative to the more rapid focused upflow in the footwall porphyries. Magmatic vapor condensing in meteoric groundwater generated acid sulfate fluids that reacted with the volcanic host rocks to produce a zoned

alteration suite typical of high-sulfidation epithermal Cu–Au–Ag deposits. Dispersed fluid flow resulted in relatively large volumes of vuggy-quartz- and alunite-quartz-altered rock. Alunite of this stage reflects equilibrium SO_4^{2-} – H_2S isotopic exchange over temperatures of 320 to 180 °C in fluids that maintained a constant redox potential and $\text{H}_2\text{S}/\text{SO}_4^{2-}$ ratio due to reaction with wallrock Fe^{2+} . During periods of high vapor influx, the hydrodynamic conditions allowed magmatic-hydrothermal fluids to displace meteoric groundwater up to the water table and to generate high-temperature (180–140 °C) low-pH (~2) steam-heated fluids with a magmatic signature. Unusually rapid SO_4^{2-} – H_2S isotopic exchange rates for this environment permitted the complete equilibration of steam-heated sulfate with H_2S at and immediately below the water table, as recorded in some steam-heated alunite. Pulses of magmatic steam from the degassing magma punctuated the deposit, but the hydrodynamic contrast at the lava-tuff contact slowed the ascent of the steam, which allowed the incorporation of groundwater and the time for partial SO_4^{2-} – H_2S isotopic exchange prior to precipitation of magmatic-steam alunite. A descending water table during the late collapse of the hydrothermal system resulted in the progressive incursion of meteoric water into the steam-heated environment, as is recorded in the isotopic composition of barite and then goethite±hematite. This oxidizing hydrothermal stage leached sulfides, redistributed metals, and possibly enriched the deposit to ore grades.

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